
International Standard



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Water quality — Determination of cyanide — Part 2: Determination of easily liberatable cyanide

Qualité de l'eau — Dosage des cyanures — Partie 2: Dosage des cyanures aisément libérables

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 6703/2 was prepared by Technical Committee ISO/TC 147, *Water quality*.

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Water quality — Determination of cyanide —

Part 2: Determination of easily liberatable cyanide

Attention is drawn to the toxicity of cyanide and to the need to take extreme care when handling cyanides and their solutions.

Carry out all operations in a fume cupboard. Avoid contact with the skin and eyes. When pipetting, always use a safety pipette (pipette by bulb). Detoxify samples and solutions containing cyanides or heavy metals in accordance with local official regulations.

Other chemicals specified in this part of ISO 6703 are also hazardous, for example pyridine.

0 Introduction

Cyanides may be present in water as hydrocyanic acid (prussic acid), as cyanide ions and as complex cyanides. They may be determined as total cyanide or as easily liberatable cyanide. If cyanide compounds are chlorinated, cyanogen chloride (CICN) is produced, and this compound has to be determined separately.

This International Standard comprises four parts as follows:

- Part 1: Determination of total cyanide
- Part 2: Determination of easily liberatable cyanide
- Part 3: Determination of cyanogen chloride
- Part 4: Determination of cyanide by diffusion at pH 6¹⁾

The method described in parts 1, 2 and 3 are suitable for controlling the quality of water and for the examination of municipal sewage and industrial effluents. They are appropriate to the technology available for the destruction of cyanides in treatment plants, and are based on the separation of liberated hydrogen cyanide (or in the case of ISO 6703/3, of cyanogen chloride) by stripping with a carrier gas.

The method specified in part 4 is suitable for the determination of smaller amounts of cyanide, depending on the concentrations of copper and nickel.

This part of ISO 6703 comprises four sections. Section one deals with the liberation and absorption of hydrogen cyanide. The other three sections deal with alternative methods for the quantitative determination of cyanide ions, as follows:

- photometric method with pyridine/barbituric acid (section two);
- titrimetric method using the Tyndall effect (section three);
- titrimetric method using an indicator (section four).

The specification of three alternative methods is necessary because each of the methods has its advantages and disadvantages. None can be quoted as applicable in all cases.

The applicability of each method is described in clauses 8, 16 and 24.

NOTE — Due to the different chemical behaviour of cyanide-containing or cyanide-producing substances, it is not possible to specify only one method for the quantitative determination of cyanide ions.

1 Scope and field of application

This part of ISO 6703 specifies three methods for the determination of easily liberatable cyanide (see clause 2) in water.

The methods are applicable to water containing less than 50 mg of easily liberatable cyanide (as cyanide ions) per litre, and less than 100 mg of total cyanide (as cyanide ions) per litre, but higher concentrations may be determined by suitable dilution of the sample.

The methods and corresponding ranges of easily liberatable cyanide contents for which they are suitable are as follows:

- Photometric method with pyridine/barbituric acid: 0,002 to 0,025 mg of cyanide;
- Titrimetric method using the Tyndall effect: > 0,005 mg of cyanide;
- Titrimetric method using an indicator: > 0,05 mg of cyanide.

A large number of ions and compounds interfere with the determination. These are listed in table 1, together with the concentrations below which they do not interfere. If present singly or in combination, up to limiting concentrations, they do not interfere with the separation of hydrogen cyanide. The list is not exhaustive.

1) At present at the stage of draft.

Table 1 — Interferences

Interference	Limiting concentration, mg/l
Sulfide ions	1 000
Polysulfide ions	500
Sulfide and polysulfide ions	1 000
Sulfide ions	500
Thiosulfate ions	1 000
Thiocyanate ions	1 000
Carbonate ions	1 000
Cyanate ions	1 000
Nitrate ions	500
Nitrite ions	500
Ammonium ions	2 000
Iron(II) and iron(III) ions	5 000
Copper(II) ions	100
Nickel(II) ions	50
Silver ions	50
Mercury ions	50
Chromate ions	300
Propionic acid	1 000
Phenol	1 000
Anthracene	100
Naphthalene	100
Anisaldehyde	10
Piperonal	10
Pyrrole	100
Pyridine	10
Chlorine (elemental)	250
Hydrogen peroxide	10
Perborate ions	10

If any of the limiting concentrations of the influences are likely to be exceeded, dilute the sample with distilled water before stabilization (see clause 6).

Prussiates (pentacyano complexes with iron), which cannot be destroyed by chlorination under normal conditions of waste water treatment, partly decompose (up to 50 %), releasing hydrocyanic acid under the conditions specified. If it is desired to exclude prussiates, the procedure specified in clause 6 and 7.1 has to be used. This procedure is only applicable, however, if the concentration of copper ions in the sample is less than 1 mg/l. The presence of aldehydes, e.g. formaldehyde, may give lower cyanide values because of the formation of cyanohydrin.

2 Definition

For the purpose of this International Standard, the following definition applies.

easily liberatable cyanide: Cyanide from substances with cyanide groups and a measurable hydrocyanic acid vapour pressure at pH 4 and room temperature.

Such substances include all cyanides which will undergo chlorination, especially hydrocyanic acid, alkali- and alkali earth metal cyanides, and complex cyanides of zinc, cadmium, silver, copper and nickel. Complex cyanides of iron and cobalt, nitriles, cyanates, thiocyanates and cyanogen chloride are not included.

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Section one: Liberation and absorption of hydrogen cyanide

3 Principle

Liberation of hydrogen cyanide from the sample by treatment at pH 4 with metallic zinc and EDTA. Entrainment of the hydrogen cyanide in a current of air into an absorption vessel containing sodium hydroxide solution.

4 Reagents

All reagents shall be of recognized analytical grade and the water used shall be distilled or deionized water.

4.1 Hydrochloric acid, solution, ρ 1,12 g/ml.

4.2 Hydrochloric acid, solution, $c(\text{HCl}) = 1 \text{ mol/l}$.

4.3 Sodium hydroxide, solution, $c(\text{NaOH}) = 1 \text{ mol/l}$.

4.4 Sodium hydroxide, solution, $c(\text{NaOH}) = 5 \text{ mol/l}$.

4.5 Tin(II) chloride, solution.

Dissolve 50 g of tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in 40 ml of the hydrochloric acid solution (4.2) and dilute with water to 100 ml.

Prepare a fresh solution each week.

4.6 Phenolphthalein, solution, containing chloroform.

Dissolve 0,03 g of phenolphthalein in 90 ml of ethanol and add 10 ml of chloroform.

4.7 Zinc- and cadmium sulfate, solution.¹⁾

Dissolve 100 g of zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) and 100 g of cadmium sulfate octahydrate ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$) in water and dilute with water to 1 000 ml.

4.8 Buffer solution, of pH 4,0.

Dissolve 80 g of potassium hydrogen phthalate ($\text{C}_8\text{H}_5\text{KO}_4$) in 920 ml of warm water.

4.9 EDTA, solution.

Dissolve 100 g of ethylenedinitrilotetraacetic acid, *d*/sodium salt dihydrate ($\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$) in 940 ml of warm water.

4.10 Zinc dust.

5 Apparatus

Usual laboratory equipment, and

5.1 Apparatus for the separation of hydrogen cyanide by stripping.

The apparatus shown in figure 1, or its equivalent, is recommended and comprises the following components.

5.1.1 Three-necked distillation flask, of capacity 500 ml, with standard conical joints (centre neck 29/32, side necks 14,5/23).

5.1.2 Reflux condenser (Liebig condenser).

5.1.3 Absorption vessels, protected against return of liquid.

5.1.4 Funnel.

5.1.5 Flowmeter.

5.1.6 Wash bottle, of capacity 250 ml, for purification of the air.

5.2 pH meter, with a glass electrode which will fit into the side necks of the distillation flask.

5.3 One-mark volumetric flasks, of capacities 25, 50, 250 and 1 000 ml.

1) Zinc salt is added to provide stable zinc hexacyanoferrates, cadmium salt is added as sulfide acceptor and because of its bactericidal effect.

Dimensions in millimetres

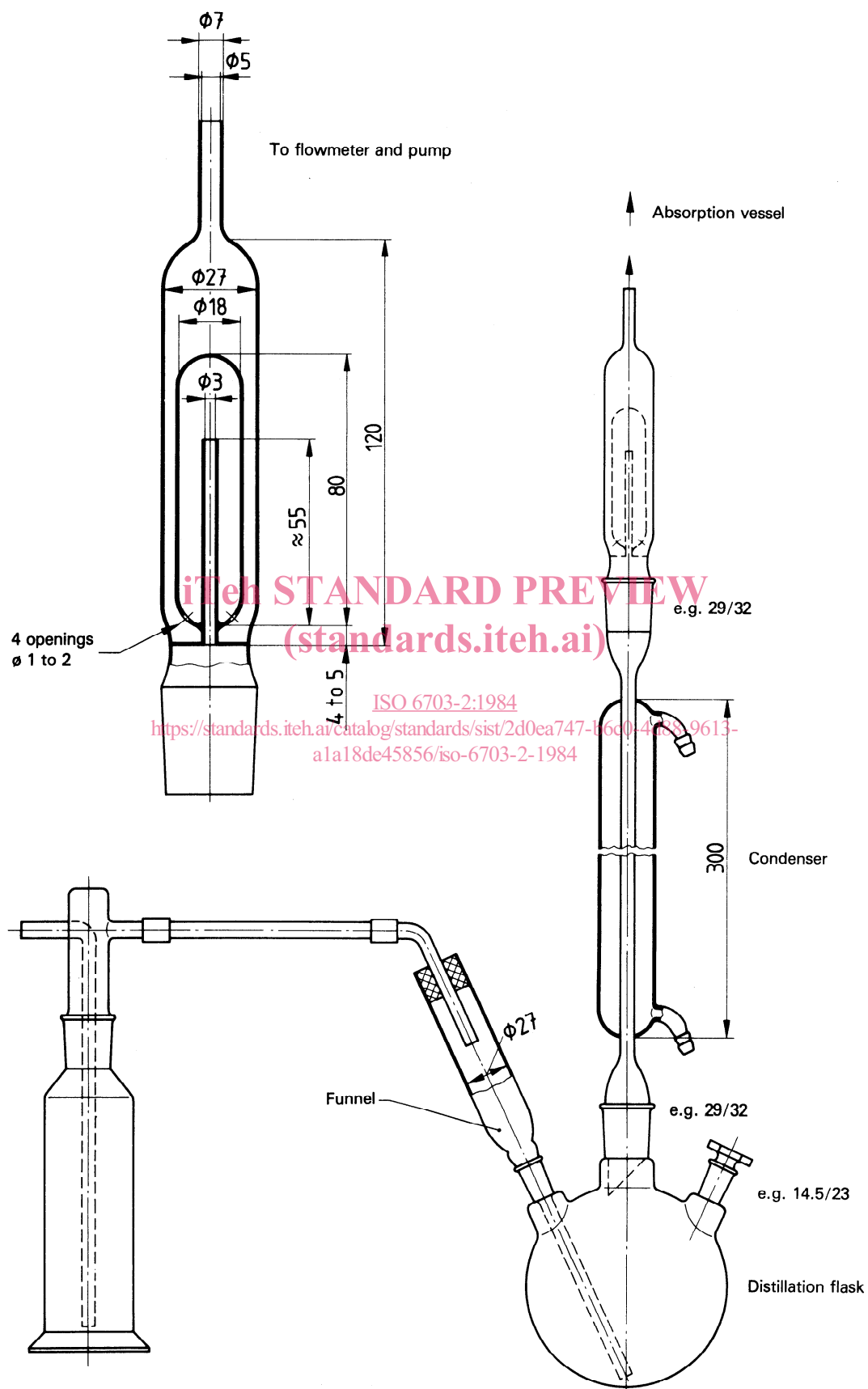


Figure 1 — Apparatus for separation of hydrogen cyanide by stripping

6 Sampling and samples

6.1 If the sample contains undissolved cyanides, it is necessary to ensure homogeneous distribution of the undissolved substances in the sample and its dilutions. Immediately after sampling, add 5 ml of the sodium hydroxide solution (4.4), 10 ml of the phenolphthalein solution (4.6) and 5 ml of the tin(II) chloride solution (4.5) to each litre of sample or diluted sample. Adjust the pH to about 8 by adding the hydrochloric acid solution (4.2), or the sodium hydroxide solution (4.3), drop by drop, until the water turns slightly red. Adjust the pH value of highly coloured samples in the same way after checking with the pH-meter (5.2) or with an indicator paper. Finally, add 10 ml of the zinc- and cadmium sulfate solution (4.8) to each litre of sample.

Analyse the sample as soon as possible. If it is necessary to store it, keep it cool and in the dark.

After addition of the zinc- and cadmium sulfate solution, a precipitate which may contain hexacyanoferrate, is formed. Accordingly, the sample should be rendered homogeneous immediately prior to taking aliquot portions. If replicate determinations are to be carried out, the aliquot portions shall be taken as quickly as possible in order to minimize any losses of gaseous hydrogen cyanide due to disturbance of the equilibrium between the gaseous hydrogen cyanide and the hydrocyanic acid in the liquid phase of the pretreated sample. If the required volume of sample is already known before sampling, it is advisable to take only this volume and to carry out the determination on the whole sample.

6.2 If prussiates are to be excluded from the determination, adjust the amount of tin(II) chloride solution (4.5) added so as to correspond to the content of oxidizing agents. The excess of tin(II) chloride solution shall be limited to 0,1 ml for each sample.

7 Procedure

7.1 Liberation and absorption of hydrogen cyanide

Pour 10 ml of the sodium hydroxide solution (4.3) into the absorption vessel (5.1.3), connect the vessel to the condenser, connect the suction tube and adjust the air flow to between 30 to 60 l/h. Pour into the distillation flask, in the following order, 10 ml of the zinc- and cadmium sulfate solution (4.8), 10 ml of the EDTA solution (4.9), 50 ml of the buffer solution (4.8) and 100 ml of the sample (see clause 6). Adjust the pH, checking by means of a glass electrode, by adding, drop by drop, the hydrochloric acid solution (4.2) or the sodium hydroxide solution (4.3), until the pH is $3,9 \pm 0,1$. Remove the glass electrode, add 0,3 g of the zinc dust (4.10)¹⁾ through the side neck and stopper the flask. Connect the wash bottle containing approximately 100 ml of the sodium hydroxide solution (4.3), to the funnel and adjust the air flow rate to 60 l/h. After 4 h, discontinue the stripping. If low cyanide concentrations (less than 0,1 mg/l) are expected, the volume of the sample may be increased to 200 ml, but the concentration of total cyanide shall not exceed 50 mg/l. In this case, increase the volumes of the zinc- and cadmium sulfate solution (4.7) to 20 ml and of the buffer solution (4.8) to 100 ml, and the amount of zinc dust (4.10) to 0,6 g.

7.2 Blank test

Carry out a blank test in parallel with the determination, proceeding as specified in 7.1 and section two, three or four as appropriate, but replacing the sample by cyanide-free water treated in the same way as the sample (see clause 6).

7.3 Quantitative determination of cyanide ions

Proceed as specified in section two (photometric method with pyridine/barbituric acid), section three (titrimetric method with end-point determination using the Tyndall effect) or section four (titrimetric method using an indicator).

1) If prussiates are to be excluded omit the zinc dust.